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ANL/CFC-18/3

Analysis of Radiolytically Generated Gases in Mini-AMORE Experiment

Chemical & Fuel Cycle Technologies Division

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Analysis of Radiolytically Generated Gases in Mini-AMORE Experiment

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1. Introduction

Argonne National Laboratory (Argonne) is assisting one of the potential domestic Mo-99 producers, SHINE Medical Technologies, as part of the National Nuclear Security Administration's (NNSA) Office of Material, Management, and Minimization (M^3) program in the development of a domestic Mo-99 production pathway that does not use highly enriched uranium (HEU). The process proposed by SHINE would produce Mo-99 by neutron-induced fission of a low enriched uranium (LEU) solution as uranyl sulfate in a subcritical assembly. As part of the development effort, Argonne is undertaking the AMORE (Argonne Molybdenum Research Experiment) project, which is essentially a pilot facility for all phases of Mo-99 production, recovery, and purification. Mini-AMORE is a part of the AMORE experiment where 2 mL samples of uranyl sulfate solution are inserted in the dry well of the AMORE target solution vessel.

Radiolysis of the water in AMORE will generate hydrogen, oxygen, and hydrogen peroxide. The rate of generation is dependent upon the power deposition into the solution with the main contribution coming from the fissioning of uranium. Hydrogen peroxide can react with the uranyl ion to form uranyl peroxide, thus forming a precipitate [1, 2]. Uranyl-peroxide precipitation must be avoided for the safe production of Mo-99 during the proposed process. The following shows the reaction of uranium and hydrogen peroxide in solution to form a precipitate:

$$UO_2^{2+} + H_2O_2 + nH_2O \leftrightarrow \downarrow UO_2O_2 \cdot nH_2O(s) + 2\ H^+$$

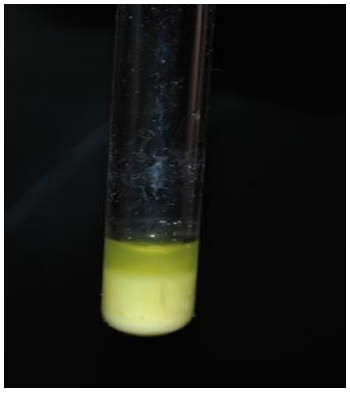

Figure 1. An LEU sample where precipitation occurred during an electron beam irradiation.

In this effort, three uranyl sulfate solutions were tested with different uranium enrichments: depleted uranium (DU, 0.267% U-235), low enriched uranium (LEU, 19.8% U-235) and high enriched uranium (HEU, 93.0% U-235). We determined the hydrogen and oxygen composition of the radiolytically generated gases that evolved from these irradiated solutions and examined them for peroxide precipitation post-irradiation.

2. Materials and Methods

2.1 Preparation of uranyl sulfate solutions

For all uranium solutions, uranium metal was oxidized to U_3O_8 and dissolved in a mixture of hydrogen peroxide and sulfuric acid with heat [3].

Table 1. Contaminant concentrations (ppm) in test solutions. (NA – not available)

Sample Type	Cr	Fe	Ni	Cu	Pt	Mn
DU	1.0	30	8.0	3.0	<0.11	N.A.
LEU	4.0	24	4.5	1.3	<0.11	1.4
HEU	1.4	19	3.1	3.8	N.A.	N.A.

2.2 Experimental setup

Drawings for the mini-AMORE capsule are shown in Figure 2. Two milliliters of a uranyl sulfate solution was placed in a quartz vial with a cap and septum (Figure 3). The septum was pierced with 1/16-in. tubing to allow a sweep gas to flow in and out of the vial. The vial was inserted into an aluminum holder (Figure 4), which served as the secondary containment. The assembly was inserted into a dry well of the AMORE target solution vessel (Figure 5). The assembly was positioned such that the solution was located near the DU target, where the maximum neutron flux occurs. Connections were made to the setup, and the system was purged with a He/Xe sweep gas. The flow of the sweep gas was controlled with a calibrated OMEGA FMA 5400-ST Mass Flow controller. The gas was analyzed using a Residual Gas Analyzer (RGA) (Pfeiffer OMNI-STAR GSD320) equipped with a 1-200 AMU PrismaPlus QMG220 mass spectrometer. The sweep gas flowed in and out of the tube carrying the radiolytic gases, hydrogen and oxygen, to the RGA analytical instrument. The RGA sampled a small portion of the gas, which exited the system through the exhaust to the Gas Collection System (Figure 6).

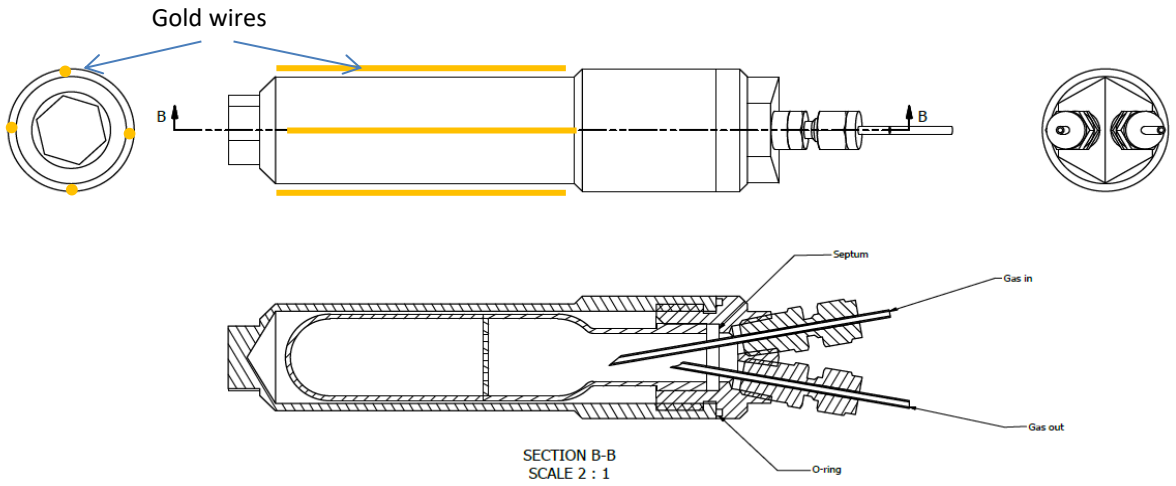

Figure 2. Drawings of the capsule for mini-AMORE irradiations.

Figure 3. Quartz vial with uranium solution

Figure 4. Aluminum secondary container

Figure 5. AMORE solution vessel with dry wells and target sleeve

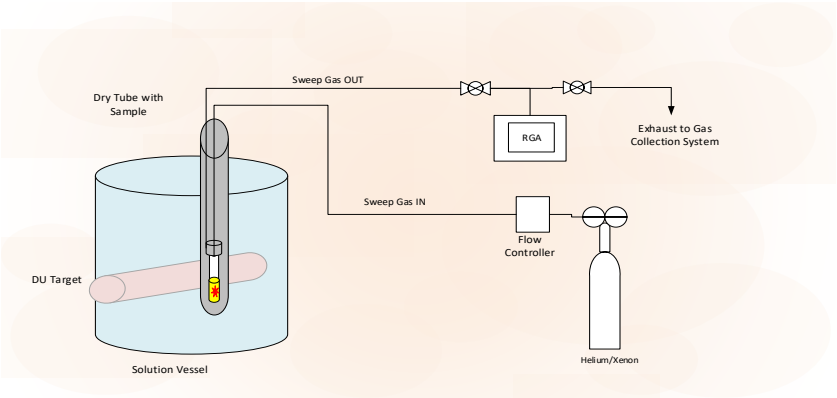

Figure 6. Experimental setup showing AMORE solution vessel with sample, sweep gas and RGA.

2.3 Gas Data Calculations

Gases that dissolved in solution were not analyzed. The solution was not continuously purged during irradiation to release the dissolved gases. A single-point calibration standard introduced at

the sampling pressure was used to calibrate the RGA. Xenon at 1.044% was used as an internal standard. Primary calibration standards were purchased with an uncertainty of ±2%. Working standards were diluted based on pressure, and helium was used as the diluent. Calibration checks performed before the experiments were within ±10% of the expected values.

The following equation was used to generate a response factor (RF) for each analyte:

$$RF = IC_{analyte} \times [IS] / IC_{IS} \times [\%Analyte] \quad (1)$$

where $IC_{analyte}$ and IC_{is} are the ion current of the analyte and internal standard, respectively, and [%Analyte] and [IS] are the concentration of the analyte and internal standard, respectively. The analyte concentration during the experiments was calculated from the following equation:

$$[\%Analyte] = IC_{analyte} \times [IS] / IC_{IS} \times RF \quad (2)$$

Background levels of nitrogen, oxygen, and hydrogen were determined from the blank sample and subtracted from the data. The oxygen values reported were corrected by subtracting a value based on the amount of nitrogen detected, which is related to the ratio of nitrogen to oxygen in air (0.2683):

$$[\%Oxygen\ Corrected] = [\%Oxygen] - [\%Nitrogen] \times 0.2683 \quad (3)$$

After the concentration of each gas was determined, the total μmoles of each analyte was calculated from the concentration data. The system was a once-through system with a He/Xe sweep gas flowing at a constant rate set by the mass flow controller. The pressure at the RGA was held constant during the experiments. The temperature at the analyzer ("room temperature") was also held constant during the experiments. The RGA sampled the sweep gas as it exited the system. The data generated by the RGA were set by the scan time per atomic mass unit of the analyte of interest, so as the RGA scans, a data point is generated for that analyte at a specified time during the analysis. The relationship between the volume of gas flowing through the system and the analysis time was used to determine the μmoles of gas generated throughout the experiment and the total generated. To that end, the ideal gas law equation was used to find the μmoles of gas detected, which was summed over the entire experiment:

$$\mu m = [PV/RT] \times [\%Analyte/100] \times 10^6 \quad (4)$$

where μm=μmoles, R=gas constant, T=analysis temperature, P=analysis pressure, and V=gas flow × time interval.

3. Results and Discussion

3.1 Gamma Counting Results

Samples were gamma counted with a high purity Ge (HPGe) detector. Activities for Zr-95, Mo-99, and Ru-103 were used to determine the number of fissions. Radioiodine activities were not used in the calculations because of its complex partitioning and volatility in acidic solution.

Gamma counting results for DU, LEU, and HEU samples are presented in Table 2. All irradiations were conducted at 40 MeV electron beam energy. Total beam energy on the target was 53 kWh (DU), 51.9 kWh (LEU), and 76.4 kWh (HEU).

Table 2. Results of the gamma counting of the mini-AMORE samples

Isotope	Half-life	Specific activity, Ci/g	Fission yield, %	DU activity, µCi	LEU activity, µCi	HEU activity, µCi
Zr-95	64.4 d	2.10E+04	6.50E+00	1.30E-01	7.85E+00	5.52E+01
Mo-99	66.2 h	4.70E+05	6.13E+00	1.12E+01	1.77E+02	1.38E+03
Ru-103	39.4 d	3.20E+04	3.10E+00	2.31E-01	6.22E+00	4.20E+01
I-131	8.04 d	1.20E+05	2.88E+00	9.64E-01	2.55E+01	6.25E+01

3.2 Neutron and Photon Flux Profiles

To obtain the neutron and high-energy photon flux profiles, we attached four gold wires to the capsule used in the HEU experiment (Figure 2). After the irradiation was complete, the gold wires were removed, cut into six pieces, and gamma counted to measure the Au-196 and Au-198 activities in the wires. The isotope Au-196 is produced by the γ,n reaction on Au-197, and Au-198 is produced from the n,γ reaction on Au-197. The Au-196 activity provides information about the photon flux distribution, and Au-198 provides information on the thermal neutron flux distribution.

Results of the activity for Au-196 and Au-198, taken at two different times after irradiation, are presented in Figure 7. Note the larger variation in the Au-196 activity compared with the Au-198 activity. This difference is as expected. Both the photon and neutron sources can be approximated as point sources, so a $1/r^2$ dependence is expected for fluxes in the vacuum. Because the solution will act as an attenuator for photons and as a moderator for neutrons, however, photon flux will fall sharper than $1/r^2$, while neutron flux will not fall as sharply. The reduced energy of the photon cross section for the nuclear reaction will increase, leading to an almost flat Au-198 activity distribution. The gold wire activation measurements showed that the fission rates in the capsule do not have a large dependence on the position of the capsule relative to the center line of the photon-neutron target.

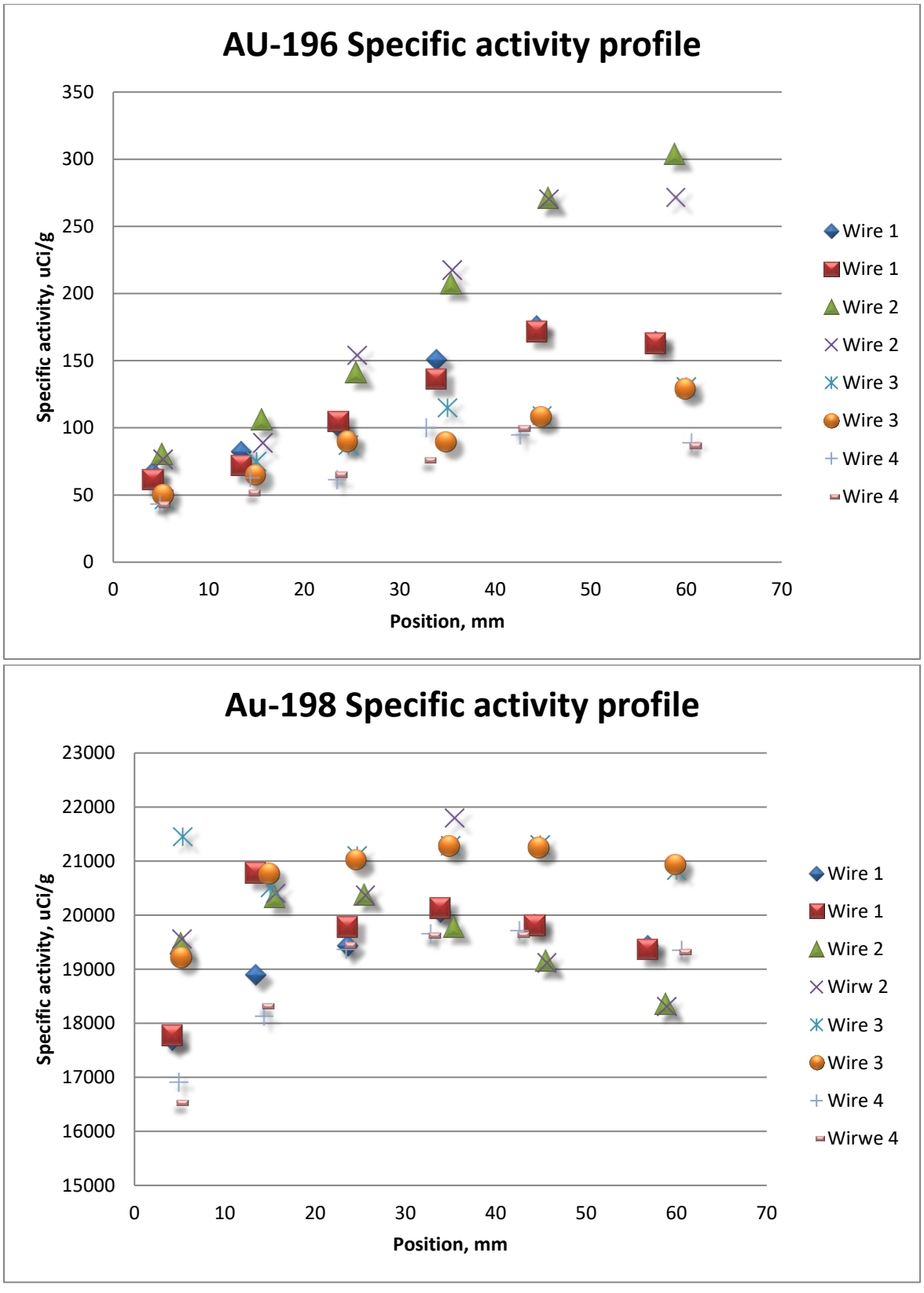

Figure 7. Distribution of Au-196 and Au-198 activities in the gold wires.

Table 3 summarizes the solution properties and irradiation conditions, including uranium concentration, percent U-235, and total beam energy. The fissions were calculated from gamma counting data based on the Zr-95, Mo-99, and Ru-103 results in Table 2. Fission energy is based on the total number of fissions, assuming an average of 200 MeV per fission. Total hydrogen and oxygen were summed over the entire irradiation, and dissolved gases were not measured.

Table 3. Summary of sample parameters, number of fissions in the samples, and total gas generation.

Date	Sample Type	U sulfate, g-U/L	U-235, %	Beam Energy, kWh	Fissions	Fission Energy, J	Total H_2, µmol	Total O_2, µmol
11/3/17	DU	152	0.267	53.0	1.44E+12	4.62E+01	19.8	5.60
11/17/17	LEU	140	19.8	51.9	3.68E+13	1.18E+03	190	67.6
1/11/18	HEU	140	93.0	76.4	2.65E+14	8.48E+03	950	357

3.3 Gas Generation Rate

Table 4 shows hydrogen and oxygen generation rates at different beam power settings (6, 12, and 18). The values for generation rate (µmol/min) were derived from Figures 8-10, which plot the sum of gas generated as a function of time. The data at each beam power setting are plotted separately. The generation rate is the slope of the plot at the particular beam power. Gas generation rates increased linearly with respect to beam power.

Table 4. Hydrogen and oxygen generation rates at different beam power.

Sample Type	H_2 generation rate at beam power, µmol/min			O_2 generation rate at beam power, µmol/min		
	6 kW	12 kW	18 kW	6 kW	12 kW	18 kW
DU	0.029	0.058	0.090	0.0050	0.017	0.022
LEU	0.31	0.61	0.74	0.10	0.22	0.29
HEU	1.6	2.7	3.5	0.59	1.0	1.3

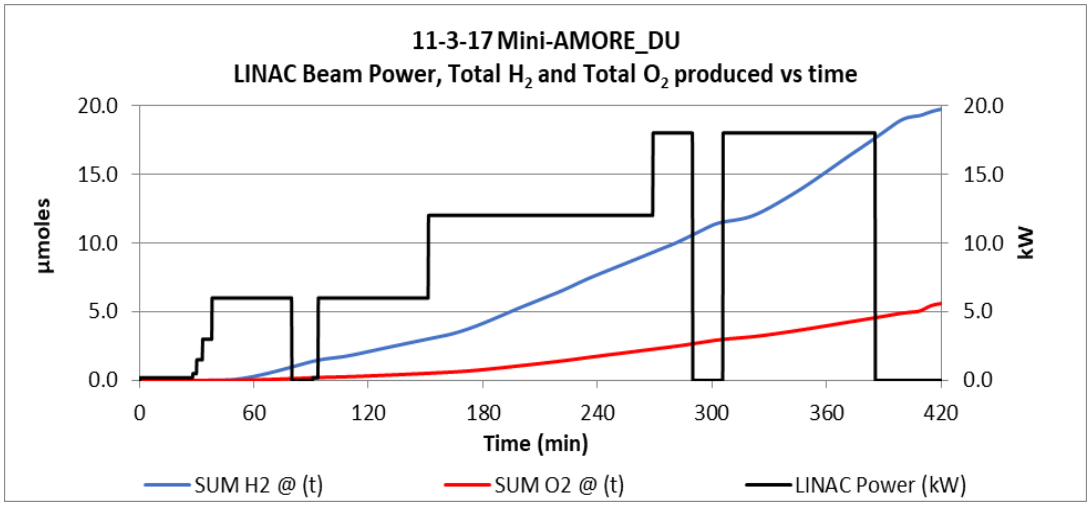

Figure 8. Total gas generation and beam power for DU experiment as a function of time.

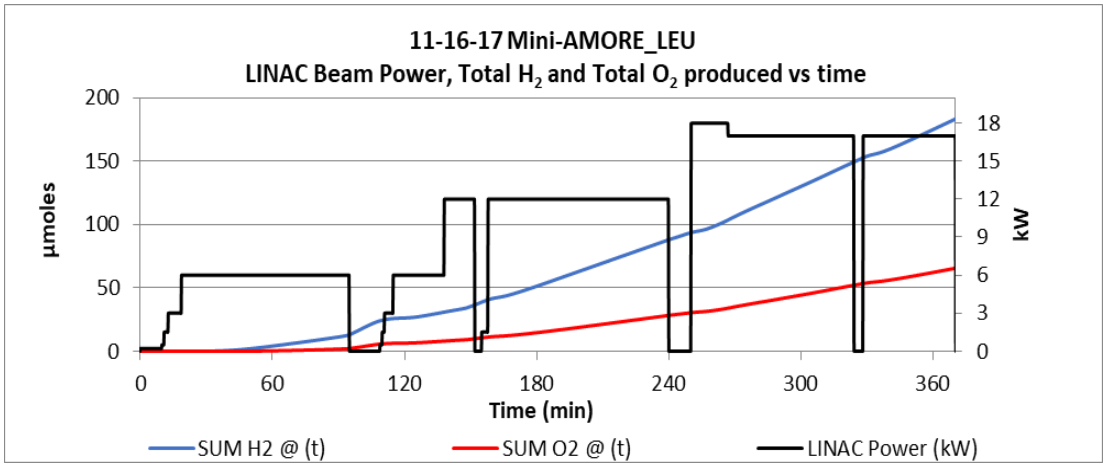

Figure 9. Total gas generation and beam power for LEU experiment as a function of time.

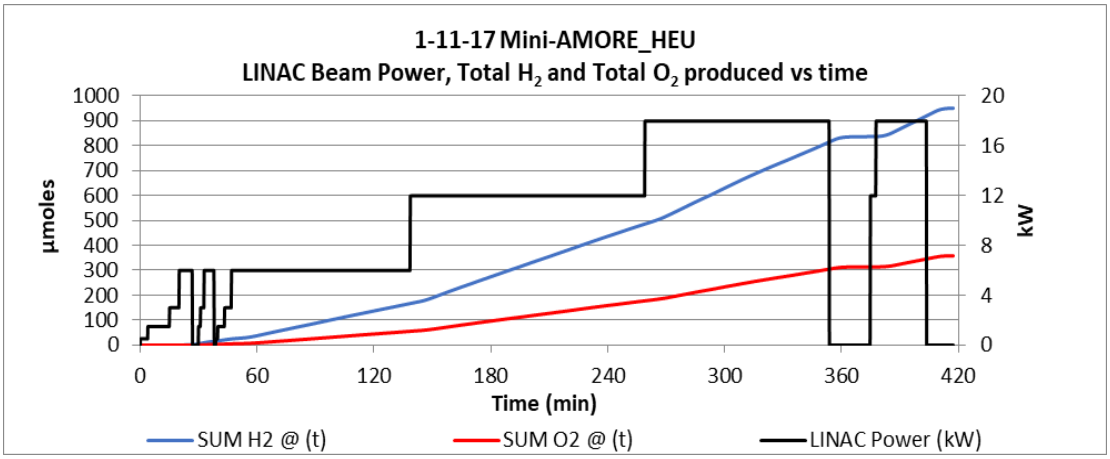

Figure 10. Total gas generation and beam power for HEU experiment as a function of time.

Figures 11 and 12 show the linear relationship of hydrogen and oxygen generation rates as a function of percent U-235.

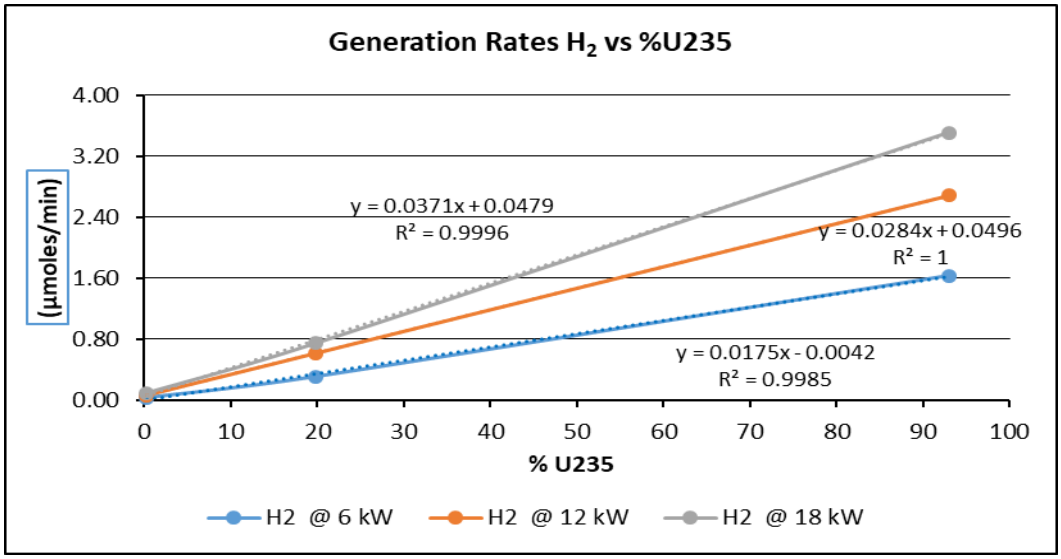

Figure 11. Hydrogen generation rate as a function of percent U-235.

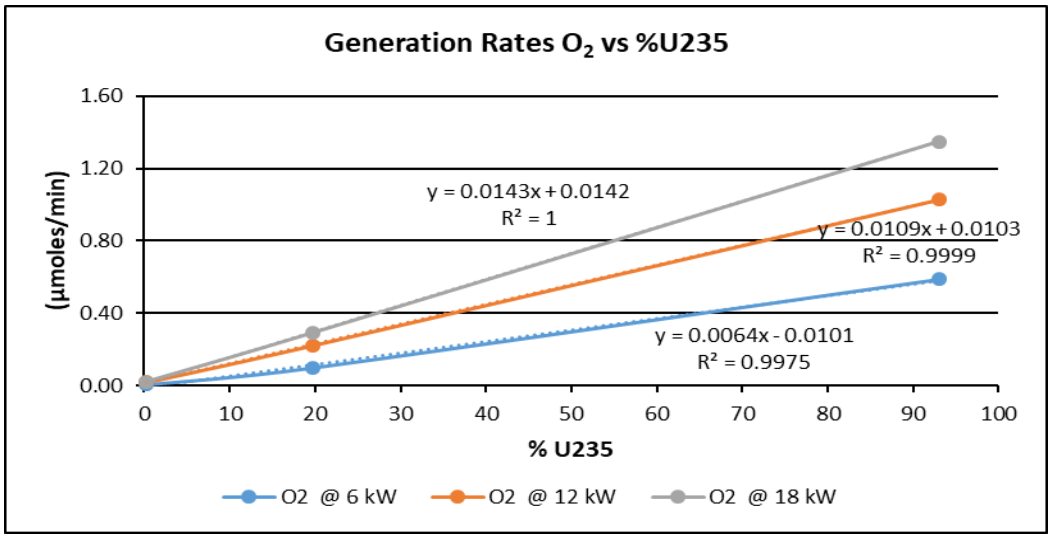

Figure 12. Oxygen generation rate as a function of percent U-235.

4. Summary

Three samples with different U-235 enrichments were irradiated as part of the mini-AMORE setup with pH 1 sulfuric acid in the target vessel. Precipitation of uranyl peroxide was not observed in these experiments. The oxygen and hydrogen generation rates from solution irradiation increased linearly with respect to beam power and percent U-235.

Radiolytic generation of hydrogen and oxygen occurs due to low and high linear energy transfer (LET) particles with different yields. The results in Figures 11 and 12 indicate that the contribution of low LET particles (photons and electrons) was similar for all enrichments, but that of the high LET particles (fission fragments) was roughly proportional to the concentration of U-235.

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[3] Youker, A., Chemerisov, S., Tkac, P., Bowers, D., Kalensky, M., & Vandegrift, G.F. "A Solution-Based Approach for Mo-99 Production: Considerations for Nitrate versus Sulfate Media." *Sci. Technol. Nucl. Install*. Article ID 402570 (2013).

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